

Characterization of a 4-miktoarm star copolymer of the (PS-*b*-PI)₃ PS type by temperature gradient interaction chromatography

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Abstract

Temperature gradient interaction chromatography (TGIC) was applied for the separation of a complex miktoarm star copolymer which has one polystyrene (PS) arm and three polystyrene-*b*-polyisoprene (PS-*b*-PI) diblock copolymer arms. Such miktoarm star polymers are much more difficult to characterize than branched homopolymers since the byproduct, typically polymers with missing arm(s) or coupled products, have not only different molecular weights but also different compositions. TGIC was able to fully separate the byproducts, and the composition of the molecular species corresponding to the different separated elution peaks was determined by two methods, fractionation/NMR and multiple detection (UV and RI). A reasonable agreement between the results of the two methods was obtained. By using the composition found, the corresponding molecular weights were determined by multi-angle light scattering detection. Based on the composition and the molecular weight we were able to identify the structure of the different molecular species.

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1. Introduction

During the last three decades, polymeric molecules consisting of several identical linear chains linked together at one chain end (symmetric stars) have attracted

the attention of scientists, since they constitute the simplest form of branching. Well-defined symmetric stars have been synthesized mainly by linking living anionic chains with multi-functional chlorosilanes [1–10]. These simple branched polymers have been used successfully to study the influence of branching on solution [11] or bulk properties [12,13]. Recently, the synthesis of stars with chemically different arms, the so-called miktoarm stars (from the Greek word μικτός meaning mixed) has been achieved [14]. The availability of miktoarm stars has facilitated studies in many fields of polymer physics and particularly in block copolymer self-assembly in selective solvents, in bulk, or on surfaces [15].

The conventional characterization of the purity of star-shaped polymers has usually been based on size

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exclusion chromatography (SEC). Although SEC coupled with various detection methods still constitutes a major tool for such analyses, SEC results are usually not sufficient to endorse the structural purity. SEC separates polymer molecules according to their hydrodynamic volume, which changes little with changing star functionality. Therefore, SEC cannot resolve the byproducts, which do not differ much in hydrodynamic volume from the major products. Other characterization methods determining the absolute molecular weight such as membrane osmometry (MO) or light scattering (LS) cannot fully complement the shortcomings of SEC.

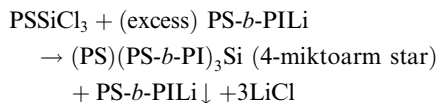
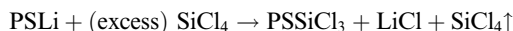
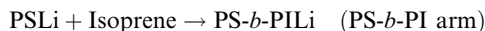
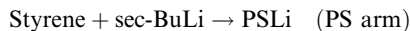
An alternative characterization method is interaction chromatography (IC). IC separation of polymer molecules is driven by enthalpic interactions of the solute molecules with the stationary phase and these interactions are, in a first approximation, proportional to the molecular weight directly. As already demonstrated with linear homopolymers, the resolution power of IC is far better than SEC [16–18]. Also IC is proven to be a powerful tool for the structural analysis of branched polymers synthesized by anionic polymerization [19–21]. Despite the use of the anionic polymerization method, it is often difficult to synthesize branched polymers with a uniform chain structure and usually various byproducts are formed. In most cases the product mixture is purified by fractional precipitation and the structural uniformity of the isolated products is examined by the conventional characterization methods including SEC, MO, and NMR. Although conventional characterization results suggest a high degree of structural homogeneity, IC analysis usually reveals the presence of significant amounts of differently branched byproducts, mainly of lower branching number [19–21].

In this study, we extend the characterization by temperature gradient interaction chromatography (TGIC) [22,23] to the case of a complex miktoarm star copolymer with one polystyrene (PS) arm and three polystyrene-*b*-polyisoprene (PS-*b*-PI) diblock copolymer arms; (PS-*b*-PI)₃PS. Such star polymers are much more difficult to characterize than branched homopolymers since the byproduct, typically polymers with missing arm(s) or coupled products, have not only different molecular weight, but also different compositions. Unlike star shaped homopolymers, one needs to determine the composition of each species in addition to the molecular weight in order to identify the molecular species in each elution peak.

2. Experimental section

2.1. Synthesis

The reaction scheme used for the synthesis of the 4-miktoarm star copolymer is as follows:



The initial step of the synthesis involved the reaction of a solution ~3% w/v of PSLi in benzene with an excess of SiCl₄ (Cl/Li ~ 200). Benzene and the excess of SiCl₄ were removed in the vacuum line. After pumping for one day, the remaining product was redissolved in benzene and the solution pumped again for two days. Finally, the product was redissolved once more in benzene and pumped for 5–6 days at 50 °C. Benzene was distilled into the reactor until a ~5% w/v solution was obtained and then a ~5% w/v solution of the PS-*b*-PILi (20% excess) in benzene was added. The linking reaction was allowed to proceed for 20 days. The progress of the linking reaction was monitored by removing samples from the reactor and analyzing them by SEC. The final product of PS(PI-*b*-PS)₃ was purified by fractional precipitation [24].

2.2. SEC and TGIC analysis

For the SEC analysis, two mixed bed columns (Polymer Lab, Mixed C, 300×8.0 mm I.D.) were used. SEC chromatograms were recorded with a multi-angle laser light scattering (MALLS, Wyatt, mini-DAWN) and a refractive index detector (Wyatt, Optilab DSP) using tetrahydrofuran (THF, Duksan, HPLC grade) as the mobile phase. Samples for analysis were dissolved in THF at an appropriate concentration (~1.0 mg/mL) and the injection volume was 100 µL. The flow rate of the mobile phase was 0.8 mL/min. The column temperature was kept at 40 °C using a column oven (Eppendorf, TC-50). Chromatograms were recorded and processed by AstraTM software.

TGIC experiments were carried out on a typical HPLC system equipped with a C18 bonded silica column (Alltech, Nucleosil C18, 100 Å pore, 250×4.6 mm I.D., 5 µm particle size). Mobile phase was 1,4-dioxane (Fisher Scientific, HPLC grade) at a flow rate of 0.5 mL/min. The polymer sample was dissolved in a portion of the elution solvent at a concentration of 3 mg/mL and the injection volume was 100 µL. The column temperature was controlled in a preprogrammed manner by circulating water from a bath/circulator (Neslab, RTE-111) through a homemade column jacket. In order to obtain absolute molecular weight and chemical composition for the sample corresponding to each TGIC elu-

tion peak, the chromatograms were recorded with a detector combination of the following sequence: a MALLS detector, a UV/Vis absorption detector (TSP, UV 100) operating at a wavelength of 260 nm, and a refractive index detector (Wyatt, Optilab DSP).

To obtain the absolute molecular weight by light scattering detection, the refractive index increment, dn/dc , was determined separately with an interferometric refractometer (Wyatt, Optilab DSP) at 690 nm. The dn/dc values of PS and PI in 1,4-dioxane obtained were 0.174 and 0.104 mL/g, respectively.

3. Results and discussion

In Fig. 1, SEC chromatograms of PS arm precursor, PS-*b*-PI arm precursor, and 4-miktoarm star copolymer are displayed. The SEC chromatograms show that the PS arm and the PS-*b*-PI arm precursors are eluted as single narrow peaks while the 4-miktoarm star copolymer shows the existence of a few easily discernible spe-

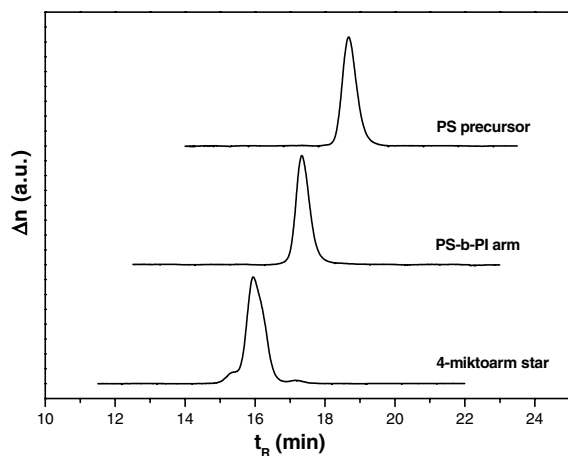


Fig. 1. SEC chromatograms of the PS arm precursor, the PS-*b*-PI arm precursor, and the 4-miktoarm star copolymer recorded with an RI detector. Column: two mixed bed columns (Polymer Lab, PL-mixed C, 300×8 mm); eluent: THF; temperature: 40 °C.

cies. The major peak at $t_R = 16$ min, representing the desired main product, PS(PS-*b*-PI)₃ star copolymer, has a conspicuous shoulder at a shorter retention time (t_R) indicating the presence of a larger sized byproduct. Also the shape of the major peak is somewhat distorted indicating that it is unlikely a single polymer species. The small peak appearing at a longer t_R around 17 min indicates the presence of a smaller sized byproduct. Judging from the retention volume, the size of the polymer species in the elution peak is between the PS-*b*-PI arm and the PS(PS-*b*-PI)₃ star copolymer. The weight and number average molecular weights (M_w , M_n) of PS precursor, PS-*b*-PI arm, and 4-miktoarm star were determined by SEC-MALLS system. The characterization results of the three samples are listed in Table 1 together with the molecular weight expected from the stoichiometry in the synthesis.

As expected, the resolution of SEC is not great because it separates polymeric materials according to hydrodynamic volume and the hydrodynamic volume of this type of star polymer does not change much with the number of arms. Therefore, it is hard for SEC to resolve small amounts of byproducts with different number of arms. IC is known to exhibit a much higher resolution for such branched polymers, and this is the reason we applied TGIC to characterize the byproducts of the miktoarm star copolymer. The right choice of a stationary phase/mobile phase pair is important for a successful IC separation. In this case C18 bonded silica and 1,4-dioxane were used for the stationary phase and mobile phase, respectively. Under these conditions, PS does not interact significantly with the stationary phase and is eluted in the SEC region (before the injection solvent elution peak) while PI is eluted in the IC regime (after the solvent peak). Therefore the retention of the PS/PI block copolymer species is determined by both total molecular weight and chemical composition. In general, the retention is mainly governed by the PI block of the molecule and generally increases as the total molecular weight of the PI increases.

Fig. 2 shows the TGIC chromatogram of the PS arm, the PS-*b*-PI arm and the 4-miktoarm star copolymer as recorded by UV absorption detector operated at 260 nm. At this wavelength only PS absorbs the light. The

Table 1

Characterization of PS arm precursor, PS-*b*-PI arm precursor, and PS(PS-*b*-PI)₃ miktoarm star copolymer by SEC-MALLS and TGIC-MALLS

Sample	M_w (kg/mol)	M_w (kg/mol)/ M_w/M_n	
	Expected	SEC-MALLS	TGIC-MALLS
PS arm	21.5	21.5/1.01	22.7/1.05 ^a
PS- <i>b</i> -PI arm	51.4	48.5/1.01	51.8/1.01
PS(PS- <i>b</i> -PI) ₃ star	176	185/1.08	

^a Separated by size exclusion mechanism.

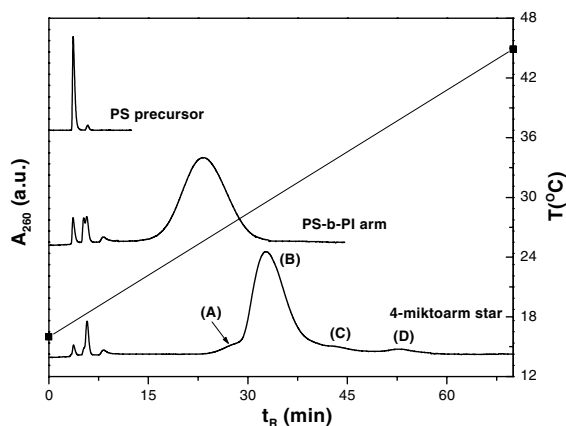


Fig. 2. TGIC chromatograms of the PS arm, the PS-*b*-PI arm and the 4-miktoarm star copolymer recorded with a UV absorption detector operated at 260 nm. Column: Nucleosil C18, 100 Å, 250×4.6 mm; eluent: 1,4-dioxane. The temperature program is shown in the plot.

temperature of the column was linearly raised from 16 to 49 °C as shown in the plot. The small peaks appearing at $t_R \approx 6$ min are the injection solvent peaks. As expected, the PS arm is eluted at very low t_R in the SEC separation regime while PS-*b*-PI arm is eluted in the IC regime. The broad peak of the PS-*b*-PI arm relative to the PS arm is due to the high resolution of IC than SEC. PS-*b*-PI arm contains a small amount of PS precursor eluted at the same t_R as the PS arm, which was not clearly observed in Fig. 1 due to the relatively broad elution peak in SEC. The other small peak appearing at $t_R \approx 8.2$ min is due to the additive (2,6-di-*tert*-butyl-*p*-cresol) added to prevent oxidation of PI. The molecular weights of the PS arm and the PS-*b*-PI arm are determined by MALLS detection and listed in Table 1 together with the SEC analysis.² The results are in good agreement each other. On the other hand, the 4-miktoarm star copolymer clearly shows the presence of at least five molecular species: a very small amount of the PS arm precursor ($t_R \approx 6$ min), a small shoulder ($t_R \approx 27$ min), a major peak ($t_R \approx 33$ min), and two small peaks ($t_R \approx 43$ and 53 min). The comparison of the TGIC chromatogram with the corresponding SEC chromatogram in Fig. 1 clearly indicates the higher resolution of TGIC than SEC. The next step is to identify the molecular species at each elution peak.

The identification of the molecular species corresponding to each elution peak for such miktoarm star

copolymers is much more complicated than for the star-shaped homopolymers since each elution peak contains molecular species that differ in chemical composition. Therefore the chemical composition of each species needs to be determined in order to calculate the molecular weight. We used two different methods to determine the chemical composition of the polymers eluted at each peak. One method is to isolate each peak by fractionation and measure the polymer composition by NMR. Although this method is straightforward and more rigorous, it is time consuming, in particular for the species of low abundance. The other method is to use multiple detectors: Each detector has different sensitivity to PS and PI. In this case we used UV absorption at 260 nm and RI detection.

$$A_{260} = a_{PI}bc_{PI} + a_{PS}bc_{PS}, \quad (1)$$

$$\Delta n = \left(\frac{dn}{dc} \right)_{PI} c_{PI} + \left(\frac{dn}{dc} \right)_{PS} c_{PS}, \quad (2)$$

where a is the absorptivity, b is the light path length and dn/dc is the specific refractive index increment. Since a and dn/dc are known for both PS and PI homopolymers, the concentration of PS portion (c_{PS}) and PI portion (c_{PI}) at each elution peak can be calculated by solving the simultaneous equations.

We first collected the three well-resolved peaks and measured the composition by ¹H-NMR. The PS content of the major peak turns out to be 49 wt%, which is in excellent agreement with the expected value of the PS(PS-*b*-PI)₃ star copolymers, 49 wt%. By using the measured composition we have calculated the dn/dc value from the relationship: $(dn/dc)_{star} = (dn/dc)_{PS}w_{PS} + (dn/dc)_{PI}w_{PI}$, and the molecular weight of the copolymer from the MALLS detector signal. Thus the molecular weight obtained was 169 kg/mol, which is again in good agreement with the expected value of the PS(PS-*b*-PI)₃ star copolymers, 176 kg/mol. Therefore we can conclude that the major elution peak corresponds to the 4-miktoarm star copolymer with the expected structure, PS(PS-*b*-PI)₃. The PS content and the molecular weight of the three resolved peaks are listed in Table 2.

From the PS content and molecular weight, the small peak (C) eluted at $t_R \approx 43$ min (43% PS content and 197 kg/mol) likely corresponds to (PS-*b*-PI)₄ star copolymer shown in Scheme 1, whose expected PS content and molecular weight are 42% and 206 kg/mol, respectively. It was most probably formed by reaction of the living PS-*b*-PI precursor with SiCl₄ remaining after the evaporation of excess SiCl₄. For the peak (D) eluted at $t_R \approx 53$ min (37% PS content and 243 kg/mol), the closest structure would be the coupled structure shown in Scheme 1 having five PS-*b*-PI arms, whose expected PS content and molecular weight are 42% and 257 kg/mol. The discrepancy would arise mainly from the small

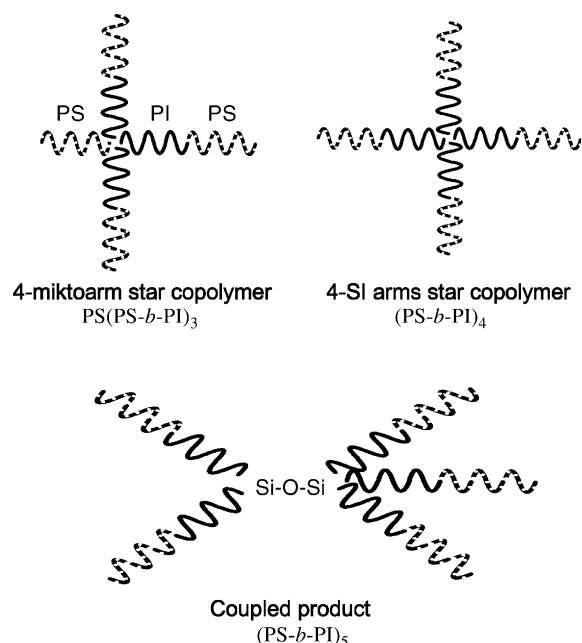
² The M_w/M_n value of the PS arm measured by TGIC is larger than SEC. This is because the PS arm is eluted at the SEC regime. Since only one C18 bonded silica column was used, the band broadening was more severe than the SEC with two mixed-bed styrene gel columns.

Table 2
TGIC characterization results of 4-miktoarm star copolymer

Peak	PS content (wt%)		M_p (kg/mol) ^a		Expected structure/PS content (wt%)/ M_w (kg/mol)	Amount (%)
	¹ H-NMR	UV & RI	¹ H-NMR ^b	UV & RI ^b		
(A)		49		122	PS(PS- <i>b</i> -PI) ₂ /52/124	2.9
(B)	49	49	169	166	PS(PS- <i>b</i> -PI) ₃ /49/176	91.1
(C)	43	39	197	199	(PS- <i>b</i> -PI) ₄ /42/206	3.7
(D)	37	35	243	250	(PS- <i>b</i> -PI) ₅ /42/257	2.3

^a Peak molecular weight determined by MALLS.

^b dn/dc values were determined by either ¹H-NMR or UV & RI.



Scheme 1. The structures of 4-miktoarm star copolymer (main product) and other branched byproducts of the synthesis.

amount of the byproducts, a large portion of which was already removed by fractional precipitation procedure. Therefore it seems highly desirable to employ TGIC before the purification step for a more accurate analysis of the byproducts. In any case, the analysis results of the composition and the molecular weight are in reasonable agreements with the structures predicted from the synthetic scheme of the miktoarm star copolymer.

Turning to the multiple-detection analysis, Fig. 3 shows the TGIC chromatograms of the 4-miktoarm star copolymer recorded by UV at 260 nm (dash line), and RI detector (solid line). The column temperature was linearly raised from 16 to 45 °C as shown in the plot. To compare the relative signal intensity of A_{260} and Δn , the delayed volume between UV and RI detectors was corrected and the heights of the UV and RI detector signal of the major peak (B) were adjusted to the same level for

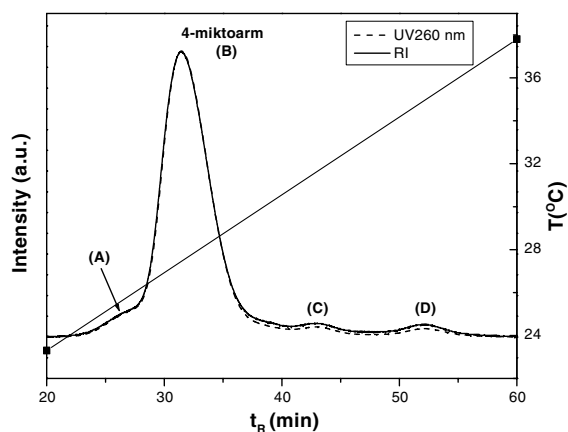


Fig. 3. TGIC chromatograms of the 4-miktoarm star copolymer recorded by a UV absorption detector at 260 nm (---), and RI detector (—). Column: Nucleosil C18, 100 Å, 250×4.6 mm; eluent: 1,4-dioxane. The temperature program is shown in the plot.

visual aid. The normalized RI chromatogram shows higher signal intensity than the UV detection chromatogram for peaks (C) and (D), while the RI and UV detection intensities are nearly the same for the peak (A). This indicates that the PS content of the peaks (C) and (D) is lower than the peak (B) since PI does not absorb light at 260 nm. From the relative signal intensity of the peaks (C) and (D) the polymer composition at each elution peak can be calculated according to Eqs. (1) and (2). The PS content of the elution peaks (A), (C), and (D) were calculated taking the 49% PS content of peak (B) as the reference. By this method, we can identify the polymer species corresponding to the elution peak (A), which was not possible to fractionate since it is eluted as a small shoulder of the intense peak (B). The PS content of peak (A) is 49% and the molecular weight is 122 kg/mol in agreement with the chain structure of PS(PS-*b*-PI)₂. The molecular weight and composition values obtained from the multiple detection method are listed in Table 2 together with the relative amount of each species and they are in fair agreement with the fractionation/NMR analysis results. Again the

discrepancy seems mainly due to the small amount of the byproducts.

In summary, we have successfully analyzed a miktoarm star copolymer with complex architecture, PS(PS-*b*-PI)₃, by TGIC. This analysis is almost impossible to perform by conventional methods such as SEC, MO, and NMR. TGIC can separate the byproducts much better than SEC. The composition of the molecular species corresponding to the different separated elution peaks was determined by two methods, fractionation/NMR and multiple detection method (UV and RI). A reasonable agreement between the two methods exists. By using the composition found, the refractive index increment of the different species was calculated and the corresponding molecular weights were determined by multi-angle light scattering detection. Based on the composition and the molecular weight we were able to identify the structure of the different molecular species.

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